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(71) Applicant
Shell Internationale Research Maatschappij B.V.

(Incorporated in the Netherlands)

Carel van Bylandtlaan 30, NL-2596 HR, The Hague,
Netherlands

(72) Inventors
Hon Chung Lau
David Roland Davies

(74) Agent and/or Address for Service
D A H Bennett
Shell Centre, 4 York Road, London, SE1 7NA,
United Kingdom

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GB 2086923 A EP 0016640 A US 4454260 A

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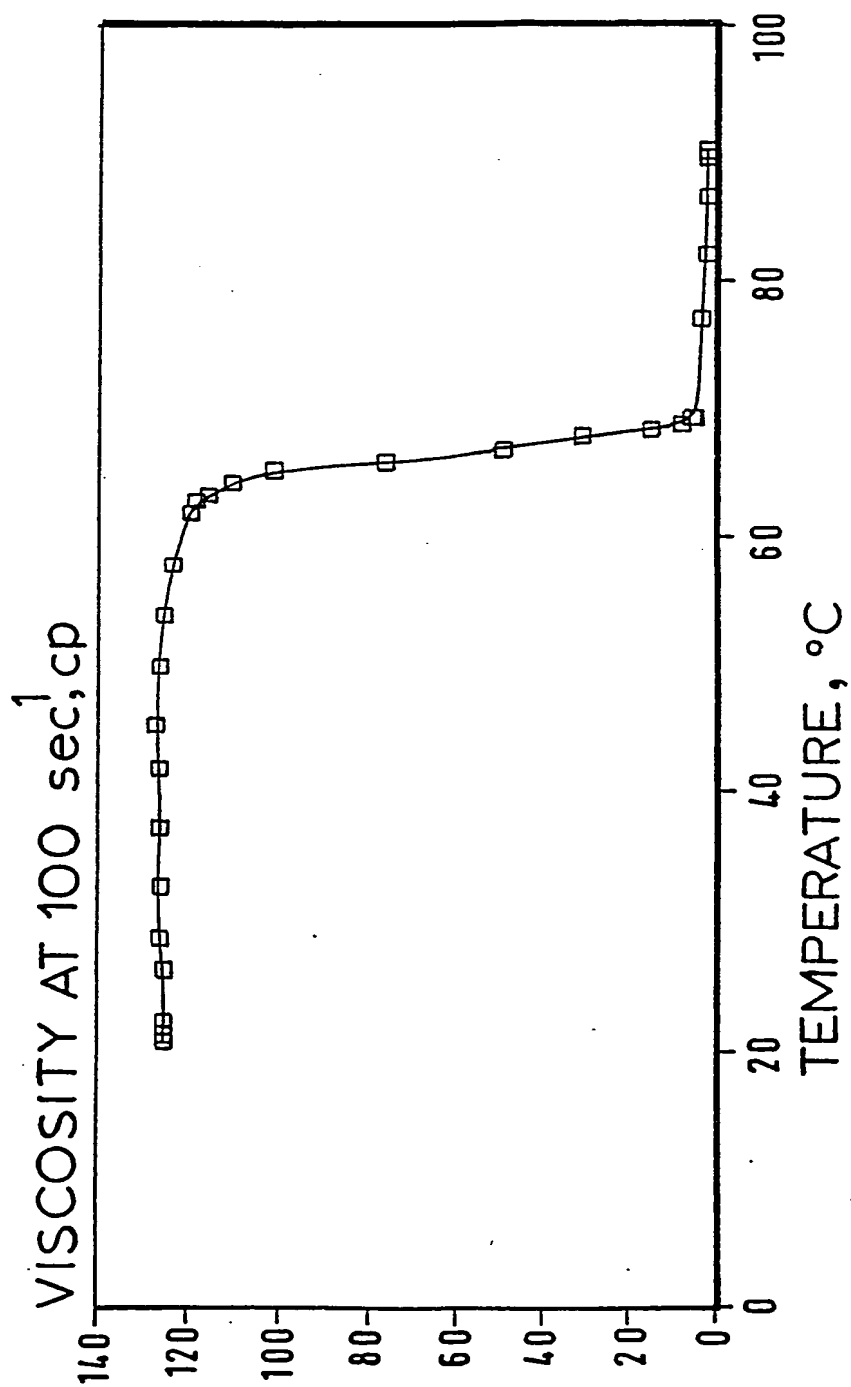
(54) Aqueous polysaccharide compositions and their use

(57) An aqueous polysaccharide composition for use in well-drilling and/or oil- and gas-recovery operations in an underground formation comprises water, a water-soluble microbial polysaccharide and an alcohol, the alcohol being present in a quantity such that the microbial polysaccharide is present in aqueous solution in the composition and the alcohol being present in a quantity such that the transition temperature of the composition is at least the temperature prevailing in the underground formation in which the composition is being used. An ionic salt and oil may be present.

GB 2 250 761 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

FIG.1



□ 0.48 % SUCCINOGLYCAN A; 2 % POTASSIUM CHLORIDE

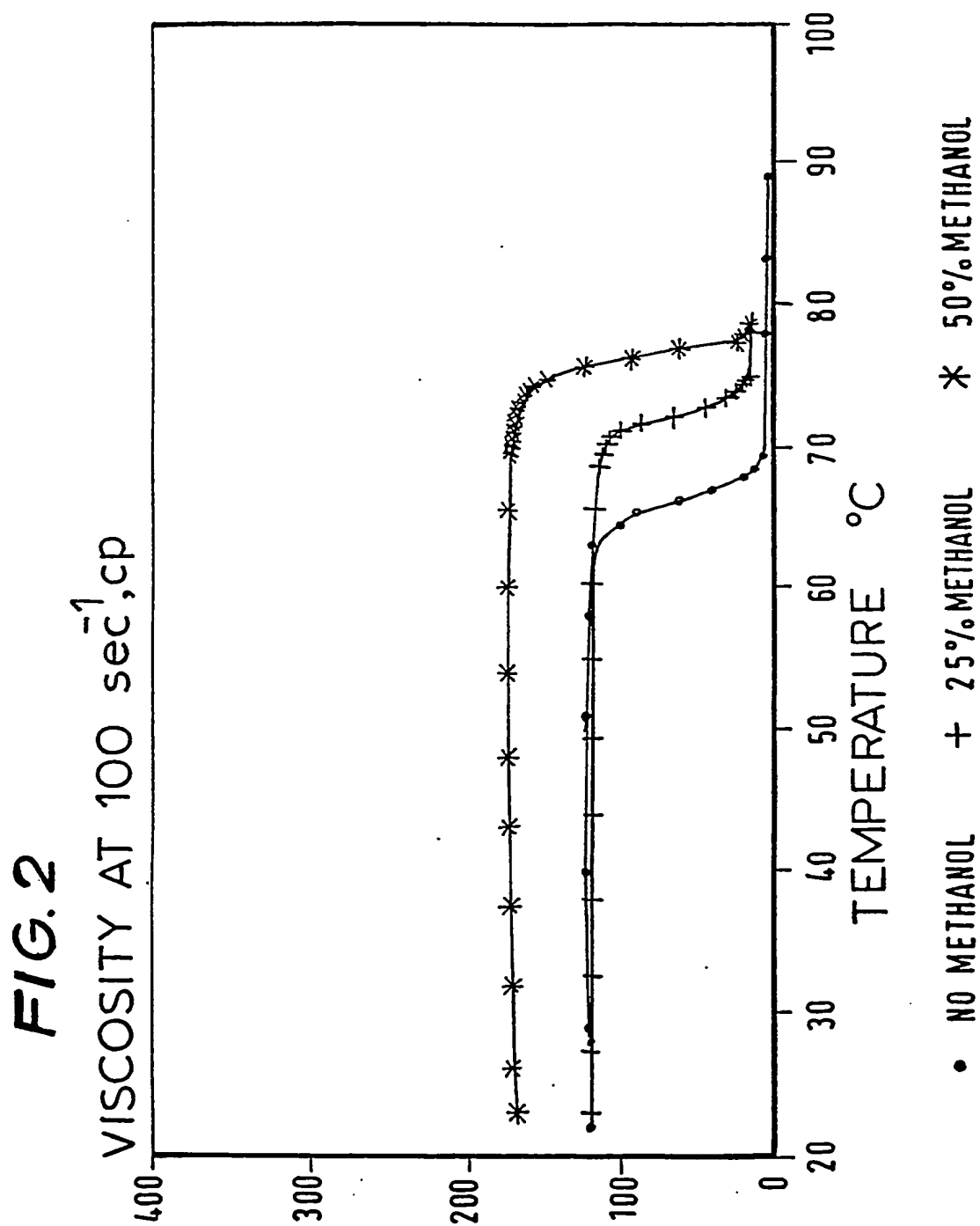
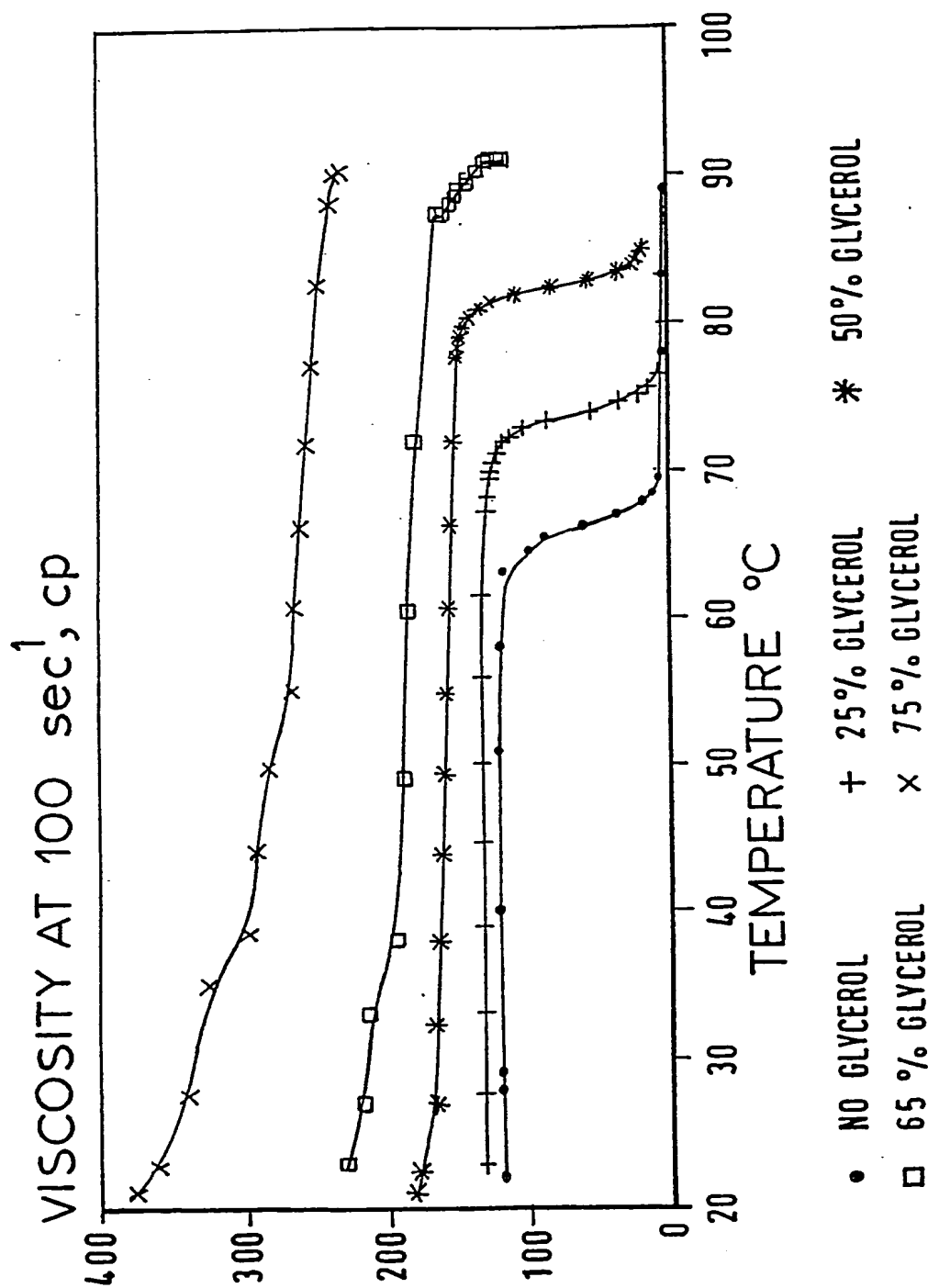


FIG. 3



- 1 -

USE OF AQUEOUS POLYSACCHARIDE
COMPOSITIONS AND AQUEOUS COMPOSITIONS

The present invention relates to the use of aqueous compositions of microbial polysaccharides in well-drilling and oil- and/or gas-recovery operations as well as to novel aqueous compositions of microbial polysaccharides.

Microbial polysaccharides, obtained by the fermentation of polysaccharide-producing microorganisms, find general use as viscosifiers. One particular area of increasing importance for the application of microbial polysaccharides is as viscosifiers for use in well-drilling and oil- and gas-recovery operations. Applications for the microbial polysaccharides in this area include use in well drilling, completion and work-over fluids, use in well fracturing techniques and use in enhanced oil and gas recovery operations.

Examples of microbial polysaccharides finding use in the aforementioned operations include succinoglycan polysaccharides, scleroglucan polysaccharides and xanthan polysaccharides.

Succinoglycan polysaccharides comprise glucose, and, for each 7 mols of glucose, 0.9 to 1.2 mols of galactose, 0.65 to 1.1 mols pyruvate, 0 to 2 mols

succinate and 0 to 2 mols of acetate, and are produced by cultivating a slime-forming species of Pseudomonas, Rhizobium, Alcaligenes or Agrobacterium, for example Pseudomonas sp. NCIB 11264, Pseudomonas sp. NCIB 11592 or Agrobacterium radiobacter NCIB 11883, or mutants thereof, as described, for example, in European Patent Application publication No. 40445 (EP-A-40445) or European Patent Application publication No. 138 255 (EP-A-138255).

Scleroglucan polysaccharides comprise linear chains of β -D-(1-3)-linked glucose residues with single glucose side chains in β -D-(1-6)-linkages, and are produced by fungi of the genus Sclerotium.

Xanthan polysaccharides typically contain mannose, glucose, glucuronic acid, O-acetyl radicals and acetal-linked pyruvic acid in molar ratio 2:2:1:1:0.5, and are produced by cultivating a species of Xanthomonas bacteria, preferably Xanthomonas campestris for example NRRL B-1459, as described, for example, in US Patent No. 4,299,825, or Xanthomonas campestris NCIB 11854, as described in European Patent Application publication No. 130647 (EP-A-130647).

Any aqueous microbial polysaccharide composition exhibits a transition temperature, above which the viscosity of the composition, as exhibited by the composition at lower temperatures, reduces dramatically. Thus, at temperatures above the transition temperature, the viscosifying power of the composition is severely reduced, if not totally lost.

Temperatures in subsurface formations increase, in general, by about 1°C every hundred feet (30 metres) of depth. Thus, a depth can rapidly be achieved in drilling operations at which the increased temperature renders a given microbial polysaccharide composition unsuitable as a viscosifier for the fluids

being employed in the operation.

There is, therefore, a need to be able to increase the range of application of a given aqueous microbial polysaccharide composition by being able to adjust the transition temperature of the composition to suit the conditions prevailing underground at a given location.

It is known that the inclusion of varying amounts of certain inorganic salts in aqueous compositions of microbial polysaccharides can alter the transition temperature of the composition.

UK Patent Application publication No. 2 167 079 (GB 2 167 079 A) discloses a process for the degradation with acid of a viscous microbial polysaccharide composition which is applied in oil and/or gas reservoir operations in which the polysaccharide composition contains an amount of a salt or a salt mixture which is sufficient to adjust the transition temperature of the composition such that it is close to the operating temperature of the reservoir. The process is said to be particularly applicable to xanthan gum preparations. The salt is preferably selected from the group consisting of salts containing chloride, bromide and iodide ions. Particularly preferred salts disclosed in GB 2 167 079 A are calcium bromide and/or zinc bromide.

A.J. Clarke-Sturman et. al. "Influence of anions on the properties of microbial polysaccharides in solution", Int. J. Biol. Macromol., 1986, Vol. 8., December, pages 355 to 360, disclose that the transition temperatures of the microbial polysaccharides succinoglycan and xanthan are strongly influenced by the salts present in solution. High concentrations of anions, such as bromide or

thiocyanate ions, lower the transition temperature of the composition. In contrast, the addition of salts, such as sulphates and phosphates, have the effect of raising the transition temperature of the composition.

Further, European Patent Application publication No. 0 259 939 (EP-A-0 259 939) discloses aqueous polysaccharide compositions comprising 0.03 to 5% w/v of a water-soluble polysaccharide, 5 to 80% w/v of at least one salt of at least one mono- or divalent cation, wherein at least 0.05% w/v, based on the composition, of the at least one salt is formate, the balance of the at least one salt, if any, being at least one halide. The inclusion of a formate salt in the composition is said in the specification of EP-A-0 259 939 to improve the thermal stability of the composition, that is, to increase the transition temperature of the composition. Particularly preferred compositions are those of xanthan polysaccharides. The compositions disclosed in EP-A-0 259 939 are stated to be useful as completion fluids, work-over fluids or drilling fluids in well drilling operations.

Finally, A.J. Clarke-Sturman et. al. "Succinoglycan: A New Biopolymer for the Oil Field", Symposium on Advances in Oil Field Chemistry, American Chemical Society, Toronto, June 5-11, 1988, pages 25 to 29 report the suitability of succinoglycan compositions for use in well completion fluids in which the partially reversible viscosity collapse of the compositions at the transition temperature is considered advantageous. It is further reported that the addition of brines, especially calcium bromide brines, to the composition has a marked effect on the transition temperature of the composition. In the case of the addition of calcium bromide brines, the

transition temperature of the succinoglycan polysaccharide composition falls. The thermal stability of the compositions can be improved, that is the transition temperature can be increased, by the addition of brines based on formate salts, such as potassium formate, which have the effect of increasing the transition temperature.

In well drilling operations and oil- and gas-producing operations of the kind discussed above, the fluids passed into the well need to be of a specific density for a given operation. The density required is determined, inter alia, by the depth of the operation and the conditions of temperature and pressure within the well. The density of the fluid being passed into the well is altered and maintained by the addition of inorganic salts, typically brines, to the fluid.

However, it has been found that the addition of inorganic salts to microbial polysaccharide compositions in the quantities sufficient to achieve the desired variations in the transition temperature of the composition, leads in turn, to a substantial variation in the density of the composition. Attempts to vary the density by the addition of further or different inorganic salts give rise to a corresponding substantial change in the transition temperature. Thus, it has been found that the hitherto known microbial polysaccharide compositions, as discussed above, are of limited application in operations where the conditions prevailing in the well require the independent variation of transition temperature and density.

Accordingly, there exists a need for aqueous microbial polysaccharide compositions which allow the density of the composition to be varied independently

of a substantial variation in the transition temperature of the composition.

Surprisingly, it has been found that the inclusion of one or more alcohols in aqueous microbial polysaccharide compositions alters the transition temperature of the composition without a substantial variation in composition density whilst allowing the density to be independently varied by the use of the conventional additives discussed above.

Compositions comprising a microbial polysaccharide and an alcohol are known. In particular, European Patent Application publication No. 0 174 689 (EP-A-0 174 689) discloses a fragrant aqueous liquid detergent composition comprising a microbial polysaccharide and industrial methylated spirit. More particularly, Canadian Patent No. 1070492 (CA 1070492) discloses an oil recovery process in which an aqueous solution of a microbial polysaccharide is treated to remove dissolved oxygen and an antioxidant and a water-soluble readily oxidizable alcohol or glycol are added and the resulting mixture injected into an underground reservoir for displacing fluids in the reservoir. Further, US Patent No. 4,717,488 (US-A-4,717,488) discloses a spacer fluid for use in oil well drilling applications comprising a slurry of 25 to 60% heteropolysaccharide, 0.5 to 6%w organophilic clay, 30 to 70%w solvent, up to 1-%w surfactant and up to 6% w methanol or isopropanol. US Patent No. 4,743,383 (US-A-4,743,383) discloses a drilling fluid additive comprising an anionic surfactant, an alcohol, a sulfonated asphalt, a microbial polysaccharide and a liquid hydrocarbon. Finally, S.L. Wellington, 55th Annv. SPE of AIME Fall Tech Conf (Dallas, 21st to 24th September, 1980) studied a range of additives for

inclusion in aqueous solutions of microbial polysaccharides to act as antioxidants, for intended use in enhanced oil recovery techniques. A great many additives were studied, selected from inorganic salts, organic acids, ureas, amides, aldehydes and alcohols.

Most surprisingly, it has been found that by varying the alcohol content of microbial polysaccharide compositions typical of the prior art, the corresponding variation in the transition temperature of the compositions is so marked that the range of operating conditions for which the composition is suitable is greatly increased.

Accordingly, the present invention provides the use in well-drilling and/or oil- and gas-recovery operations in an underground formation of a polysaccharide composition comprising water, a water-soluble microbial polysaccharide, an alcohol, optionally an ionic salt, and optionally an oil; the alcohol and ionic salt, if present, being present in a quantity such that the microbial polysaccharide is present in aqueous solution in the composition and the alcohol being present in a quantity such that the transition temperature of the composition is close to the temperature prevailing in the underground formation in which the composition is being used. - Preferably the transition temperature is at least the temperature prevailing in the underground formation. The difference between the transition temperature and the temperature of the underground formation is usually between 0 to 20°C, preferably between 5 and 15°C.

It will be appreciated from the above that the invention also relates to the compositions which are to be used in well drilling and/or oil- and gas-recovery operations and which are novel in respect

to the prior art. These polysaccharide compositions comprise water, at least one water-soluble microbial polysaccharide, an alcohol optionally an ionic salt, and optionally an oil, the alcohol and the ionic salt, if present, being present in a quantity such that the microbial polysaccharide is present in aqueous solution in the composition, and the alcohol being present in an amount between 20 and 90% wt, preferably between 25 and 85% wt, still more preferably between 40 and 80% wt.

The composition may comprise any water-soluble microbial polysaccharide, for example a succinoglycan polysaccharide, a scleroglucan polysaccharide or a xanthan polysaccharide. Xanthan and succinoglycan polysaccharides are preferred for the compositions of the present invention, with succinoglycan polysaccharides being especially preferred.

The microbial polysaccharide is present in the composition in the quantity necessary to provide the required viscosity of the composition. Preferably the microbial polysaccharide is present in an amount from 0.1 to 2% wt, more preferably 0.25 to 0.75% wt.

Alcohols for inclusion in the composition preferably have from 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms, especially 1 to 6 carbon atoms. The lower molecular weight alcohols having from 1 to 3 carbon atoms are particularly preferred.

The alcohol may be any alcohol or a mixture of alcohols. Very satisfactory variation in the transition temperature can be achieved by the inclusion in the composition of a mono-alcohol, that is, a water-miscible compound bearing a single hydroxy substituent. Preferred mono-alcohols are methanol,

ethanol and propanol. Methanol is a particularly preferred mono-alcohol.

However, preferred alcohols for inclusion in the compositions are poly-alcohols. The term "poly-alcohols" as used herein is a reference to a water-miscible organic compound bearing a plurality of hydroxy substituents. Very satisfactory variation in the transition temperature of the composition may be obtained by the inclusion of a diol as the organic solvent. Examples of suitable diols for use in the composition include ethylene glycol (ethane-1,2-diol), diethylene glycol (2,2'-oxydiethanol) and propane-1,2-diol. Preferably, the poly-alcohol bears at least 3 hydroxy substituents. Examples of such poly-alcohols include glycerine or glycerol (Propane-1,2,3-triol). Alternatively, the polyalcohol may be one of the ethers of glycerol, for example diglycerol, hexaglycerol or decaglycerol. Mixtures of the ethers of glycerol may be used. One preferred mixture of ethers is polyglycerol or polyglycerine.

Glycerol and polyglycerol are particularly preferred alcohols for inclusion in the compositions.

The lower molecular weight alcohols for inclusion in the composition exist as liquids at ambient conditions, whilst the higher molecular weight alcohols may exist as solids at ambient conditions. Both liquid and solid alcohols are suitable for inclusion in the composition, with liquid alcohols being preferred.

The alcohols for inclusion in the compositions are available commercially, for example ex Aldrich Chemie N.V., Brussels, Belgium.

The alcohol is included in the composition in the amount necessary to achieve the required variation in the transition temperature of the composition. The

maximum possible amount of the alcohol present in the composition is determined by the concentration of alcohol at which the microbial polysaccharide is caused to precipitate out from the aqueous solution.

The maximum concentration of alcohol possible before precipitation of the microbial polysaccharide occurs varies according to the particular microbial polysaccharide and, if present, the particular ionic salt. For a given composition, this concentration can be readily determined by experimental methods using standard laboratory techniques available to persons skilled in the art. Concentrations of alcohol in the composition of up to 90% wt and above are possible, depending upon the particular alcohol concerned. The alcohol is preferably present in an amount between 20 and 90% wt, more preferably between 25 and 85% wt, still more preferably between 40 and 80% wt.

The advantageous feature of the compositions is that the inclusion of the alcohol in the composition allows a significant variation in the transition temperature of the composition to be achieved without an associated substantial change in the density of the solution. Thus, it is possible to further include in the compositions one or more ionic salts to achieve a variation in density. Whilst, as taught by the prior art discussed above, the inclusion of an ionic salt in an aqueous microbial polysaccharide composition has an effect on the transition temperature of the composition, this effect is substantially overwhelmed by the effect on transition temperature due to the presence of the alcohol. Thus, by varying the concentrations of the alcohol and the ionic salt an independent variation in the transition temperature and density of the composition can be achieved.

Thus, the compositions may optionally comprise one or more ionic salts. Suitable ionic salts include any of those heretofore known and used in the art. Examples of suitable ionic salts include those having cations selected from the group consisting of ammonium, barium, caesium, calcium, lead, lithium, magnesium, manganese, potassium, rubidium, silver, sodium, strontium, thallium and zinc. Calcium, sodium, potassium and zinc are very convenient cations. Examples of suitable anions for the ionic salt include halide ions, particularly chloride and bromide, formate, sulphate, phosphate, hydrogen phosphate, thiocyanate and salicylate. Chloride, bromide, formate, phosphate and sulphate are very convenient anions. Potassium chloride is a very convenient ionic salt.

It will be apparent to those skilled in the art that incidental quantities of other ionic salts, for example nitrates and bicarbonates, may also be present in compositions of the invention, and will be present in compositions in which sea water, or other naturally occurring brine, is used in preparing the composition.

The amount of ionic salt present in the composition will be determined by the required density of the composition. Typically, the ionic salts may be present in an amount of from 0 to 50% wt, preferably from 0 to 20%wt.

In certain applications, for example those described by T.O. Allen and A.P. Roberts, Production Operations, Volume 2, Well Completions, Workover and Stimulation, 2nd Ed., 1982, pages 134 to 136, the compositions may advantageously be applied in the form of oil-in-water emulsions, with the microbial polysaccharide, alcohol and ionic salts being present in solution in the aqueous phase of the emulsion.

Suitable oils for inclusion in such oil-in-water emulsions include those oils known and used in the art.

In addition to the aforementioned advantages offered by the compositions, it has also most surprisingly been found that the inclusion of an alcohol in an aqueous microbial polysaccharide solution has the effect of increasing the viscosity of the composition at given conditions of temperature and shear rate. This has the advantage that lower concentrations of the microbial polysaccharide are required in compositions which comprise an alcohol in order to achieve the required viscosifying effect.

The aqueous microbial polysaccharide composition may be prepared by mixing an alcohol with an aqueous composition containing the water-soluble microbial polysaccharide, with, when present, the ionic salt and the oil. It is preferred to dissolve the microbial polysaccharide in the aqueous phase and then add the alcohol and, if required, the ionic salt. However, the order of incorporation of components may be adapted to each specific polysaccharide, alcohol, salt formulation.

The composition may be used, for example, as a completion fluid, a work-over fluid, a gravel-pack fluid, a fluid loss control fluid, a hydraulic fracturing fluid, an acid fracturing fluid or a drilling/underreaming fluid in a well-drilling operation or in an oil and/or gas recovery operation.

The compositions may be applied in the form of aqueous solutions of the microbial polysaccharide in association with the other components and optional components hereinbefore described.

Alternatively, the compositions may be applied in the form of the oil-in-water emulsions hereinbefore described.

The compositions find particular use in fluids in the hydraulic fracturing of underground formations. For such use, compositions comprising a succinoglycan polysaccharide are especially preferred.

In hydraulic fracturing operations, underground formations adjacent the well are caused to fracture by the application in the well of a fluid under a high pressure. The resultant fractures within the formations promote the production of oil from the well. Fluids applied in such operations may advantageously comprise a composition according to the present invention.

Hydraulic fracturing may require the inclusion in the fluids of various solids, or proppants, such as gravel. In the hydraulic fracturing operation, the proppant is transported as a suspension in the fluid to the fracture formation where it enters the fractures and serves to prevent subsequent closure of the fractures. The compositions of the present invention are of particular advantage for inclusion in fluids for use in such operations. The transition temperature of the composition may be varied to lie close to the operating temperature within the well. This initially allows effective transport of the proppant within the well to the fractured formation to be achieved. The subsequent inevitable heating of the fluid within the well then leads to a reduction in the viscosity as the transition temperature of the composition is exceeded, facilitating cleaning of the well and finally removal of the fluid from the well. In some operations, it has been found advantageous to coat the particles of proppant in resin, such that

they bind together once situated in the fractured formation within the well. Such techniques are taught for example in Petroleum Abstracts, Vol 30, No. 9, 3rd March, 1990, abstract No. 477810, reference 3.

Compositions which comprise a succinoglycan polysaccharide have been found to be particularly advantageous for use with such resin-coated proppants.

The present invention will be further understood from the following illustrative examples and their associated figures, in which Examples 1 is a comparative example.

Example 1

An aqueous solution of the commercially available succinoglycan polysaccharide "SHELLFLO-S" (trade mark), hereinafter referred to as "succinoglycan A", was prepared at a concentration of 0.48% wt polysaccharide. Sufficient potassium chloride was added to the polysaccharide solution with stirring at ambient temperature (21°C) to achieve a concentration of 2% wt ionic salt. A sample of the resulting solution was heated at 90°C over a period of 1.5 hours in a contraves 115 Couette viscometer at a shear rate of 100 sec⁻¹. The viscosity of the solution was measured continuously throughout the heating period. The transition temperature was determined by a sharp decrease in the viscosity of the solution being tested. The solution exhibited a transition temperature of 66°C. The viscosity of the solution at ambient temperature (21°C) was 0.127 Pa.s at a shear rate of 100 sec⁻¹. The viscosity of the solution at a temperature of 30°C was 0.121 Pa.s at a shear rate of 100 sec⁻¹. The solution had a density of 1000 kg/m³.

The results of the viscosity measurements taken

during the heating period are represented graphically in Figure 1.

Examples 2 to 6

The general procedure of Example 1 was followed to determine the effect of a variety of mono-alcohols at varying concentrations on the transition temperature of aqueous solutions of succinoglycan A. The results are set out in Table 1, together with the results of Example 1 for comparison purposes.

The results of the viscosity measurement for compositions containing methanol taken during the heating period are represented graphically in Figure 2.

It can be seen from the data of Table 1 and from Figure 2, that a marked variation in transition temperature of the composition was achieved with a minimal accompanying variation of no more than 10% in the density of the composition.

Table 1

Example No.	Additive to 0.48 % wt succinoglycan A solution	Transition Temperature (°C)	Viscosity at 100 sec ⁻¹ (ambient) temperature (Pa.s)	Density (kg/m ³)
1	Potassium Chloride 2% wt	66	0.127	1000
2	Methanol 25% wt Potassium Chloride 2% wt	72	0.126	960
3	Methanol 50% wt Potassium Chloride 2% wt	76	0.183	950
4	Ethanol 50% wt	74	0.092	920
5	1-Propanol 50% wt	74	0.110	900
6	2-Propanol 23.4% wt Potassium Chloride 2% wt	68	0.128	-

Examples 7 to 14

The general procedure of Example 1 was followed to determine the effect of a variety of poly-alcohols, bearing two or three hydroxy substituents, at varying concentrations on the transition temperature of aqueous solution of succinoglycan A. The results are set out in Table 2, together with the results of Example 1 for comparative purposes.

The results of the viscosity measurements for compositions containing glycerol taken during the heating period are represented graphically in Figure 3.

From the data in Table 2 and from Figure 3 it can be seen that the inclusion of a poly-alcohol bearing two or three hydroxy substituents gave rise to a wide variation of transition temperatures of the composition with only a minimal variation in the density of the composition. Further, the data of Table 2 indicates that an increase in solution viscosity at the indicated rates of shear was achieved by the inclusion of the poly-alcohols in the composition, as compared with the comparative example, Example 1.

Table 2

Example No.	Additive to 0.48 % wt succinoglycan A solution	Transition Temperature (°C)	Viscosity at 100 sec ⁻¹ (ambient) temperature (Pa.s)	Density (kg/m ³)
1	Potassium Chloride 2% wt	66	0.127	1000
7	1,2-Propanediol 50% wt Potassium Chloride 2% wt	79	0.200	1050
8	Ethylene Glycol 50% wt Potassium Chloride 2% wt	80	0.152	1070
9	Diethylene Glycol 50% wt Potassium Chloride 2% wt	82	0.208	1110
10	Glycerol 25% wt Potassium Chloride 2% wt	74	0.146	1060

Table 2 (continued)

Example No.	Additive to 0.48 % wt succinoglycan A solution	Transition Temperature (°C)	Viscosity at 100 sec ⁻¹ (ambient) temperature (Pa.s)	Density (kg/m ³)
11	Glycerol 50% wt Potassium Chloride 2% wt	83	0.210	1130
12	Glycerol 65% wt Potassium Chloride	91	0.258	-
13	Glycerol 75% wt Potassium Chloride 2% wt	> 91	0.431	-
14	Glycerol 25% wt Potassium Formate 5% wt	76	0.153	1070

Example 15

The general procedure of Example 1 was followed to determine the effect on transition temperature of including the poly-alcohol polyglycerol in an aqueous solution of succinoglycan A. The composition was prepared as an aqueous solution having the following components:

Succinoglycan A	0.48% wt
Potassium Chloride	2.0% wt
Polyglycerol	25% wt

The composition exhibited a transition temperature of 74°C. The density of the composition was 1080 kg/m³ at ambient temperature. The viscosity of the composition was 0.171 Pa.s at a shear rate of 100 sec⁻¹ and at ambient temperature.

Again, a substantial variation in transition temperature was achieved with minimal variation in the density of the composition, whilst also achieving an enhanced viscosity at the measured shear rates, compared with the comparative composition of Example 1.

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CLAIMS

1. Use in well-drilling and/or oil- and gas-recovery operations in an underground formation of a polysaccharide composition comprising water, a water-soluble microbial polysaccharide, an alcohol, optionally an ionic salt, and optionally an oil; the alcohol and the ionic salt, if present, being present in a quantity such that the microbial polysaccharide is present in aqueous solution in the composition and the alcohol being present in a quantity such that the transition temperature of the composition is close to the temperature prevailing in the underground formation in which the composition is being used.
2. Use according to claim 1, characterised in that the transition temperature of the composition is at least the temperature prevailing in the underground formation.
3. Use according to claim 1, characterised in that the alcohol is a poly-alcohol.
4. Use according to claim 3, characterised in that the poly-alcohol is glycerol or polyglycerol.
5. Use according to any preceding claim, characterised in that the alcohol is present in an amount between 20 and 90% wt.

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6. Use according to claim 5, characterised in that the alcohol is present in an amount between 25 and 85% wt, preferably between 40 and 80% wt.
7. Use according to any preceding claim, characterised in that the microbial polysaccharide is selected from succinoglycan polysaccharides, scleroglucan polysaccharide and xanthan polysaccharides.
8. Use according to claim 7, characterised in that the microbial polysaccharide is a succinoglycan polysaccharide.
9. Use according to any preceding claim, characterised in that, the microbial polysaccharide is present in an amount of from 0.1% wt to 2% wt.
10. Use according to any preceding claim, characterised in that the ionic salt is selected from salts having a calcium, sodium, potassium or zinc cation.
11. Use according to any preceding claim, characterised in that the ionic salt is selected from salts having a chloride, bromide, formate phosphate or sulphate anion.
12. Use according to claim 10 or 11, characterised in that the ionic salt is potassium chloride.
13. Use according to any preceding claim, characterised in that the ionic salt is present in an amount of from 0 to 50% wt.
14. Use substantially as hereinbefore described having reference to any one of Examples 2 to 15 or to either of Figures 2 or 3.
15. Use according to any preceding claim, characterised in that the composition is used as a completion fluid, a work-over fluid, a hydraulic fracturing fluid, an acid fracturing

fluid or a drilling fluid in a well drilling operation or in an oil and/or gas recovery operation.

16. Polysaccharide composition comprising water, at least one water-soluble microbial polysaccharide, an alcohol, optionally an ionic salt, and optionally an oil, the alcohol and the ionic salt, if present, being present in a quantity such that the microbial polysaccharide is present in aqueous solution in the composition, and the alcohol being present in an amount between 20 and 90% wt, preferably between 25 and 85% wt, still more preferably between 40 and 80% wt.
17. Polysaccharide composition according to claim 16, to be used in well drilling and/or oil- and gas-recovery operations.
18. Polysaccharide composition as hereinbefore described with reference to any one of the Examples 2 to 15 or to either Figures 2 or 3.

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Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

9026596.8

Relevant Technical fields

(i) UK CI (Edition K) E1F (FGP, FMB, FPA);
 C3U (UFB, UFZ)

(ii) Int CI (Edition 5) C08L; C09K; E21B

Search Examiner

D B PEPPER

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

14 FEBRUARY 1992

Documents considered relevant following a search in respect of claims

1 TO 18

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2086923 A (NL INDUSTRIES) see page 1, lines 57 to 61 & page 2, lines 5 to 39	16,17
X	EP 0016640 A (MERCK) see page 2, lines 9 & 22 to 31	16,17
X	US 4454260 A (DAWANS ET AL) see column 2, line 67 to column 3, line 13 & column 4, lines 50 to 53	16,17

SF2(p)

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Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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